Electronic Supplementary Material (ESI) for RSC Advances.

† Electronic supplementary information (ESI)

S.1. Hansen Solubility Parameters (HSP)

HSP is based on the concept of "like dissolves like". Each molecule is given three Hansen parameters, δ_D, δ_P and δ_H, the energy from dispersion forces, dipolar intermolecular forces, and hydrogen bonds between molecules, respectively. These parameters can be considered as coordinates of a point ($\delta = \sqrt{\delta D^2 + \delta P^2 + \delta H^2}$) in the so-called Hansen space. The HSP distance between two molecules, R, is a measure of how alike they are. The smaller the R, the more likely they are to be compatible ($R(HSP) = \sqrt{4(\delta D1 - \delta D2)^2 + (\delta P1 - \delta P2)^2 + (\delta H1 - \delta H2)^2}$).[1]

S. 2 Materials and Chemicals

Spun plain woven polyester fabric #777H (PET) was purchased from Testfabrics, Inc. (West Pittiston, PA. Benzoyl peroxide (BPO), tert-butyl proxy benzoate (tBPB), di-tert-butyl peroxide (DtBP), and 2-Acrylamido-2-methyl-1-propane sulfonic acid (AMPS), were purchased from Sigma- Aldrich chemical company Inc. (Milwaukee, WI). N-methyl-2-pyrrolidone (NMP), N-butyl salicylate (BS), ethyl benzoate (EB), toluene (Tol), and Tetramethyl-4-piperidinyl methacrylate (TMPM) and were supplied by Fisher Scientific (Houston, TX). An emulsifier, Tergitol XJ was purchased from the Lab Depot, Inc (Dawsonville, GA).

S.3. Preparation of grafting solutions

The composition of the grafting solution and the curing condition are based on the optimum conditions attained from a factorial design approach.[2] Table S1 shows the chemical compositions and curing condition.

Since initiators selected for the reaction are water-insoluble, first the initiator and monomers were mixed well with 10 mMol emulsifier, Tergitol XJ (Dow chemical), until a homogeneous paste was obtained at room temperature. Then 10% (v/v) organic solvent was added to the paste and mechanically stirred until it results in a clear solution to which then distilled water was added gradually under high speed stirring. At this level a homogeneous stable grafting emulsion is formed.

Table S1- Chemical compositions and curing condition

Solution	**Initiator Conc. in mMol (wt%)**	**Monomer Conc. In mMol (wt%)**	**Emulsifier in mMol (wt%)**	**Solvent in vol% (wt%)**	**Temp. (C)**	**Time (min)**
1	100 (2.4)	TMPM-300 (6.8)	10 (2.6)	10 (10.05)	160	5
2	100 (2.4)	AMPS-300 (6.2)	10 (2.6)	10 (10.05)	160	5

S.4. Thermo-induced radical graft polymerization

Pre-washed fabric samples were dipped in the grafting system and then padded. The wet pick-up rate of all samples was controlled around 100%. Padded fabrics were directly cured without additional drying in an oven at an elevated temperature for a certain period of time. All treated samples were then thoroughly washed in detergent solution at 60 C° for 20 min, rinsed vigorously with distilled water, acetone and distilled water again to remove all unreacted monomers and homo-polymers. Samples were dried at 60°C and then conditioned in a standard environment (21 ^{o}C and 65% relative humidity) overnight before weighing measurements.

The surface grafting is evaluated using different measures such as 1) the grafting yield ($GY\ (mmole/g) = ((W_3 - W_1) \times 1000)/(M \times W_1)$), where W_1 is the weight of samples before grafting, W_3 is the weight of washed grafted samples, and M is the molecular weight of the monomer. For the grafting yield to be comparable for different monomers it is defined as mMole weight increase after grafting per one gram of the original sample, and 2) relative moisture regain ($RMR\ (\%) = (Ww - Wd)/Ww \times 100$). For this purpose the samples were placed in an oven at 55 C° for 24 hours and their weight was recorded (W_d). Then samples were placed in a desiccator with water instead of a desiccant at room temperature for 24 hours (W_w).

Supplement Table S2 shows HSP distances from PET, chemical structures and half-lifetime of four peroxide radical initiators, benzoyl peroxide (BPO), tert-butyl proxy benzoate (tBPB), di-cumyl peroxide (DCP), and di-tert-butyl peroxide (DtBP). Supplement Tables S3 and S4 show

HSP distances from PET and chemical structures of four organic solvents (N-methyl-2-pyrrolidone (NMP), N-butyl salicylate (BS), ethyl benzoate (EB), and toluene (Tol)) and two selected monomers (Tetramethyl-4-piperidinyl methacrylate (TMPM) and 2-Acrylamido-2-methyl-1-propane sulfonic acid (AMPS)). HSP values for PET are: δ_D=18.8, δ_P=11.9, δ_H=4.5. Two main attributes were considered in the selection of initiators: 1) having strong affinity towards PET backbone. Thus Hansen Solubility Parameter (HSP) Software was used to calculate the HSP distances as an indicator of affinity to PET, and 2) appropriate half-lifetime under the desired curing temperature. The rate of radical formation is characterized by the half-lifetime ($t_{1/2}$) of the peroxide under a temperature. Half-lifetime ($t_{1/2}$) of different initiators were calculated using the Arrhenius equation $K_d = Ae^{\wedge}(- E_a/RT)$, $t_{1/2} = ln2/K_d$ where K_d is the rate constant for initiator dissociation (s^{-1}), A, Arrhenius frequency factor (s^{-1}), E_a is the activation energy for the initiator dissociation (J/mole), R=8.3142 (J/mole-K), and T is the temperature (K).

Table S2- HSP distances, Chemical structures, and half lifetimes of peroxide initiators

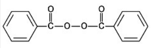
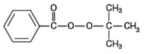
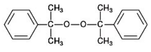
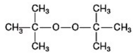
initiator	**HSP distance from PET**			**Chemical Structure**	**Condition (min/C)**
	δ_D	**δ_P**	**δ_H**		
Benzoyl Peroxide (BPO)	2.1				160/3
	18.9	9.8	4.6		
tert-Butyl Proxy Benzoate (tBPB)	7.0				160/5
	17	7	8		
Di-Cumyl Peroxide (DCP)	9.3				170/5
	17.5	3.1	6.1		
Di-tert-Butyl Peroxide (DtBP)	12				180/5
	14.6	3.8	7.2		

Table S3- HSP distances, and Chemical structures of solvents

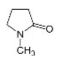
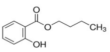
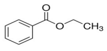
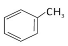
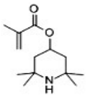
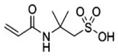
Solvent	**HSP distance from PET**			**Chemical Structure**	**Boiling point (°C)**
	δ_D	**δ_P**	**δ_H**		
N-Methyl-2-pyrrolidone (NMP)	2.8				202-204
	17.8	3	3.7		
N-Butyl Salicylate (BS)	5.9				268
	18	7.4	7.9		
Ethyl Benzoate (EB)	6				211-213
	17.8	6.3	4.1		
Toluene (Tol)	9.2				111
	18.1	10.6	6.6		

Table S4- HSP distances and Chemical structures of monomers

Monomers	**HSP distance from PET**			**Chemical Structure**
	δ_D	δ_P	δ_H	
Tetramethyl-4-piperidinyl methacrylate (**TMPM**)	10			
	16.3	3.3	3.5	
2-Acrylamido-2-methyl-1-propane sulfonic acid (**AMPS**)	16.0			
	18.4	19.3	18.7	

S. 5. Characterization

Fourier transform infrared (FTIR) spectroscopy measurements for all samples were carried out using a Nicolet 6700 FTIR spectrophotometer (Thermo Electron Co., USA) by using KBr pellets with acquisition conditions of spectral range of 4000−400 cm−1, resolution at 4 cm−1, and 64 accumulations. The samples were made thin enough to ensure that the Beer-Lambert law was fulfilled.

Surface morphologies of both grafted and control samples were observed by using a scanning electron microscope (SEM) (XL 30-SFEG, FEI/Philips, USA) at 15 kV accelerating voltage on gold sputter coated samples with backscattered electron (BSE) detector.

A handheld digital microscope, Dino-Lite (USA) was used to take images from the dyes samples after grafting.

The surface elemental analyses of the grafted samples were characterized by energy dispersive X-ray spectroscopy (EDS) (INCA system, Oxford) at 5kV acceleration voltages. Samples were coated with gold (about 20 nm).

References

1. C. M. Hansen, *Hansen Solubility Parameters:A User's Handbook,* 2nd ed.; CRC Press: Boca Raton, Fl, 2007.
2. D. C. Montgomery, *Design and Analysis of Experiments*, 8th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2012.